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*Theorem Concerning the Effect of Discrete Charges in the
Electrical Double Layer*

*II. The Apparent Anomaly in the Rate of Change with
Concentration of the Potential of the Electrocapillary Maximum*

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Technical Report

Number 13

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January, 1954

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Department of Chemistry

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THEOREM CONCERNING THE EFFECT OF DISCRETE CHARGES IN THE ELECTRICAL DOUBLE LAYER

by

David C. Grahame

ABSTRACT

In contradiction to a theorem advanced earlier by Esin and Shikov, it is here demonstrated that a uniform array of discrete oriented dipoles generates a potential difference no different from that associated with two uniform layers of charge having the same average charge density.

According to the argument here presented, it is not possible to explain a supposed anomaly in the rate of change of the potential of the electrocapillary maximum with concentration as an effect attributable to the discrete character of the charges which go to make up the adsorbed layer of anions in the electrical double layer.

An analogous argument is presented for the case of a charged sphere carrying a discrete layer of oriented dipoles.

INTRODUCTION

There is a supposed anomaly in the way in which the potential of the electrocapillary maximum (e.c.max.) of mercury varies with the concentration of surface-active electrolytes such as potassium iodide (1-3). Briefly, what is found is that the potential of the e.c.max. sometimes varies more rapidly than 59 millivolts per ten-fold change of concentration, whereas this figure represents an upper limit to the rate of change considered possible according to classical double layer theory.

Esin and Shikov (1) suggest that this anomaly is related to the fact that adsorbed ions do not behave like a smeared-out layer of charge and that account must be taken of the discrete nature of the electrical charges centered on the adsorbed ions. They have derived an expression which purports to represent the potential across a layer of discrete dipoles arranged in hexagonal array with the positive ends of the dipoles lying in one plane and the negative ends in another, parallel to the first. It is our opinion that the Esin and Shikov derivation is in error for a number of reasons which will not

be stated in detail since we are about to derive a general theorem which makes their mode of treatment of the problem unnecessary.

The theory of Esin and Shikov did not account for the anomalous variation of the potential of the e.c.max. with concentration in a quantitative manner. Ershler (2) subsequently modified their theory considerably, while still using their equation for the potential of a layer of discrete dipoles.¹ Although it is claimed that the Ershler theory accounts for the facts in a quantitative manner, it is the contention of the present author that this can not be so because the fundamental concept is unsound.

COMPARISON OF POTENTIALS GENERATED BY DISCRETE AND CONTINUOUS LAYERS OF CHARGE

Consider an infinite plane layer of oriented dipoles arranged in hexagonal or any other regular array. It is to be understood that the dipoles consist of two point charges (+e and -e) separated by a distance γ . The positive ends of the dipoles lie in one plane and the negative ends in the other.

The potential ψ at a distance s from the nearer plane is given by the expression

$$\psi = \sum_{i=1}^{\infty} \frac{e}{D(r_i^2 + s^2)^{3/2}} - \sum_{i=1}^{\infty} \frac{e}{D[r_i^2 + (s+\gamma)^2]^{3/2}} \quad (1)$$

where r_i is the distance of the i th charge (one end of a dipole) from a point in the plane opposite the point whose potential is sought (Fig. 1). D is the dielectric constant, assumed constant. The individual sums in expression 1 increase without limit, but their difference is finite. This is easily seen by calculating corresponding quantities for two smeared-out planes of charge. In that case the potential is given by

$$\psi = \int_0^m \frac{2\pi\rho r dr}{D(r^2 + s^2)^{3/2}} - \int_0^m \frac{2\pi\rho r dr}{D[r^2 + (s+\gamma)^2]^{3/2}} \quad (2)$$

where ρ is the surface charge density and r is the radius of the incremental annular ring of charge. m is the limit of r , regarded for the moment as finite. Therefore after integration

¹. It appears to us that Ershler has somewhat modified Esin and Shikov's equation also, but since neither the original equation nor Ershler's modification of it seems to us to be correct, the difference does not affect the present discussion. See footnote 2, however, for a further discussion of Ershler's equation.

Infinite plane layers of discrete charges

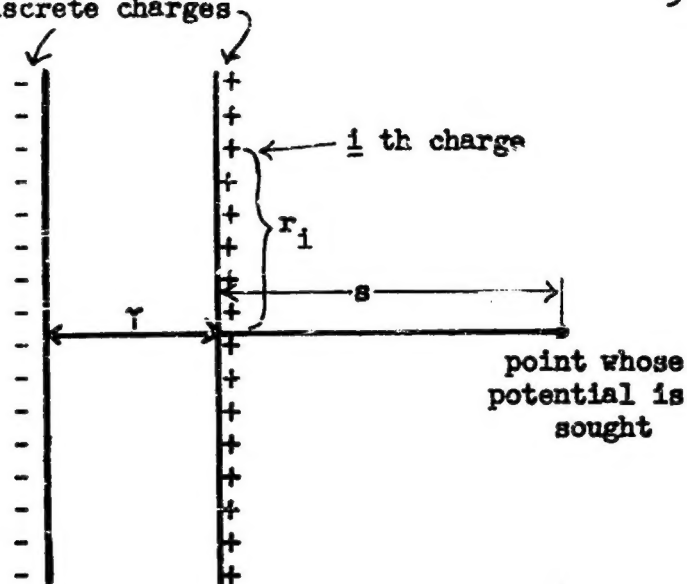


Fig. 1. Schematic representation of two layers of charge or one layer of oriented discrete dipoles.

$$\psi D/2\pi = (m^2 + s^2)^{1/2} - [m^2 + (s + \gamma)^2]^{1/2} + \gamma \quad (3)$$

For finite values of m , ψ is a function of m and s as well as of γ . As m increases without limit, each of the square roots increases without limit, but their difference goes to zero, as one can show by factoring out m and expanding the remaining factor. Thus in the limit $\psi = 2\pi\epsilon\gamma/D$. To the left of the two planes the potential is $-2\pi\epsilon\gamma/D$ (or in any case opposite in sign from the potential on the right) making the overall potential difference $4\pi\epsilon\gamma/D$, as one could have deduced easily from the familiar relation $d\psi/dx = 4\pi\epsilon/D$.

It is instructive to plot the potential ascribable to each plane of charge separately, although both potentials are infinite, so that all one can really represent is the rate of change of the potential with distance. This is done in Fig. 2.

The distance between the parallel lines of potential gives the potential at any point. The special advantage of this diagram is that it makes it possible to analyze the corresponding problem for a layer of discrete dipoles (now regarded as two layers of discrete charges) without evaluating the difficult summations presented by equation 1. Each summation in equation 1 is divergent, as already stated, but the summations are symmetrical about the planes to which they refer and differ only in sign. Therefore the potential diagram corresponding to Fig. 2 for this case will be as shown in Fig. 3. The exact shape of these curves can only

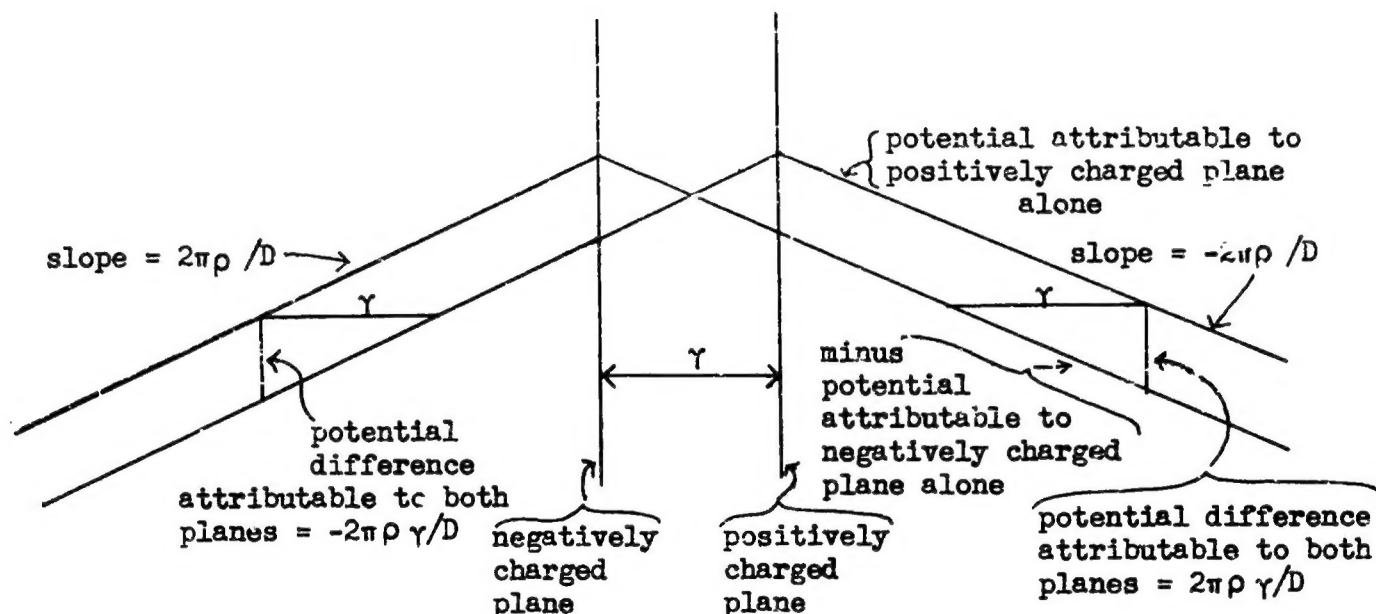


Fig. 2. Schematic representation of potentials attributable to each plane singly in a pair of uniformly charged infinite planes. Vertical distance between sloping lines represents potential difference attributable to both planes at once.

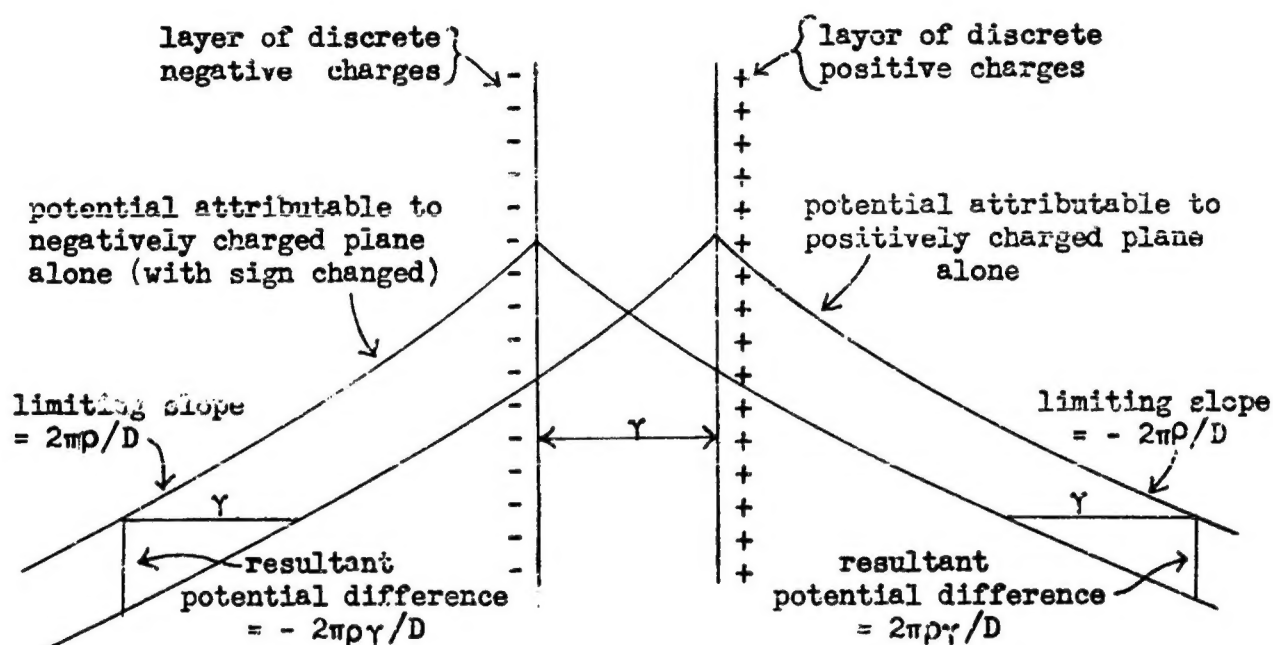


Fig. 3. Schematic representation of potentials attributable to each plane singly in a pair of parallel layers of uniformly arranged discrete charges or oriented discrete dipoles.

be established by explicit summation of the terms in equation 1, and this turns out to be a difficult mathematical task because of the very slow convergence. It could be solved without difficulty by the use of present day high speed computing methods, but this has not been done because it proves to be unnecessary. It is physically obvious that the effect of the discreteness of charge upon the slope of the curves in Fig. 3 diminishes as the distance from the planes is taken to be ever greater. Therefore the limiting slope of these curves must be the same as in Fig. 2, namely $\pm 2\pi\rho/D$ where ρ is the average charge density on the planes of charge.

This being the case, the distance between the curves must be $2\pi\rho\gamma/D$ on both sides of the figure, making a total potential difference attributable to the layers of discrete charge $4\pi\rho\gamma/D$, which is just the value found for two layers of smeared-out charge. It is concluded, therefore, that the total potential difference attributable to a layer of discrete oriented dipoles is the same as for smeared out charges. This is in contradiction to the findings of Esin and Shikov and of Ershler.

Since one does not in reality deal with infinite sheets of charge, it is worth while noting briefly how this argument applies to the more usual case of concentric charged spheres. One can draw potential diagrams similar to those shown in Figs. 2 and 3 which have the added advantage that the potentials are not infinite. Thus for uniformly distributed smeared-out charges elementary considerations lead to the following diagram (Fig. 4)

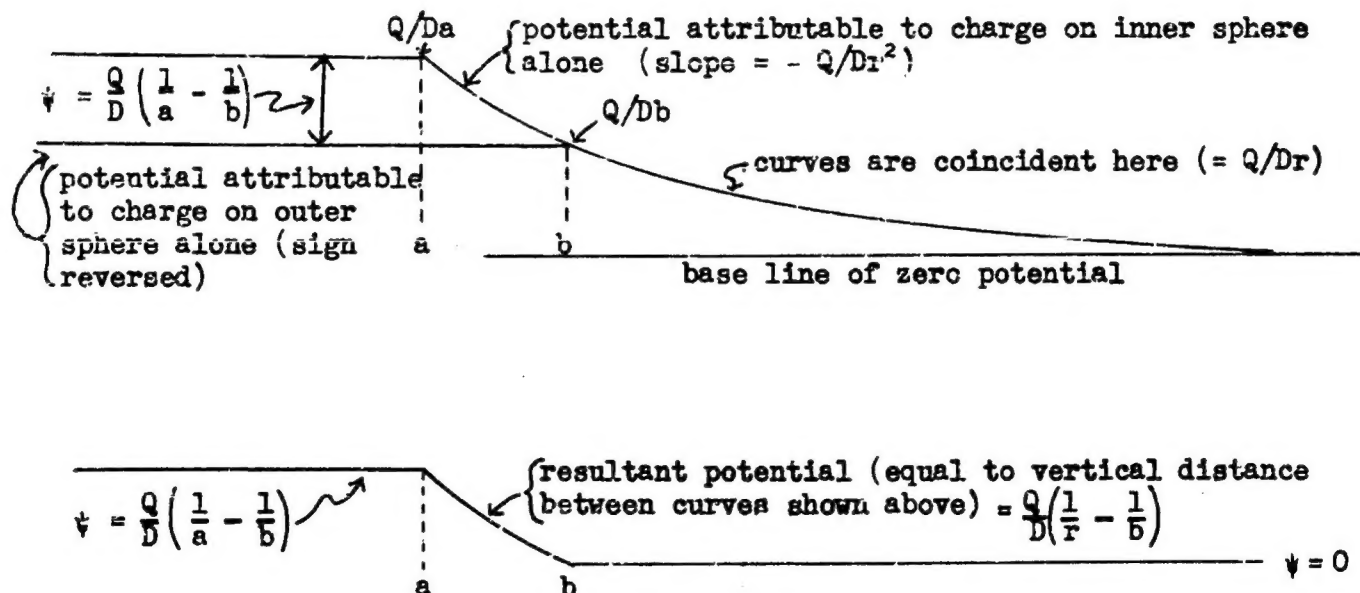


Fig. 4. Schematic potential diagrams for uniformly distributed charges on two concentric spheres.

where a and b are the radii of the two concentric charged spheres and Q and $-Q$ are their respective charges. r is the distance of an arbitrarily chosen point from the center of the two spheres.

Corresponding diagrams for two layers of discrete charge will be as shown in Fig. 5.

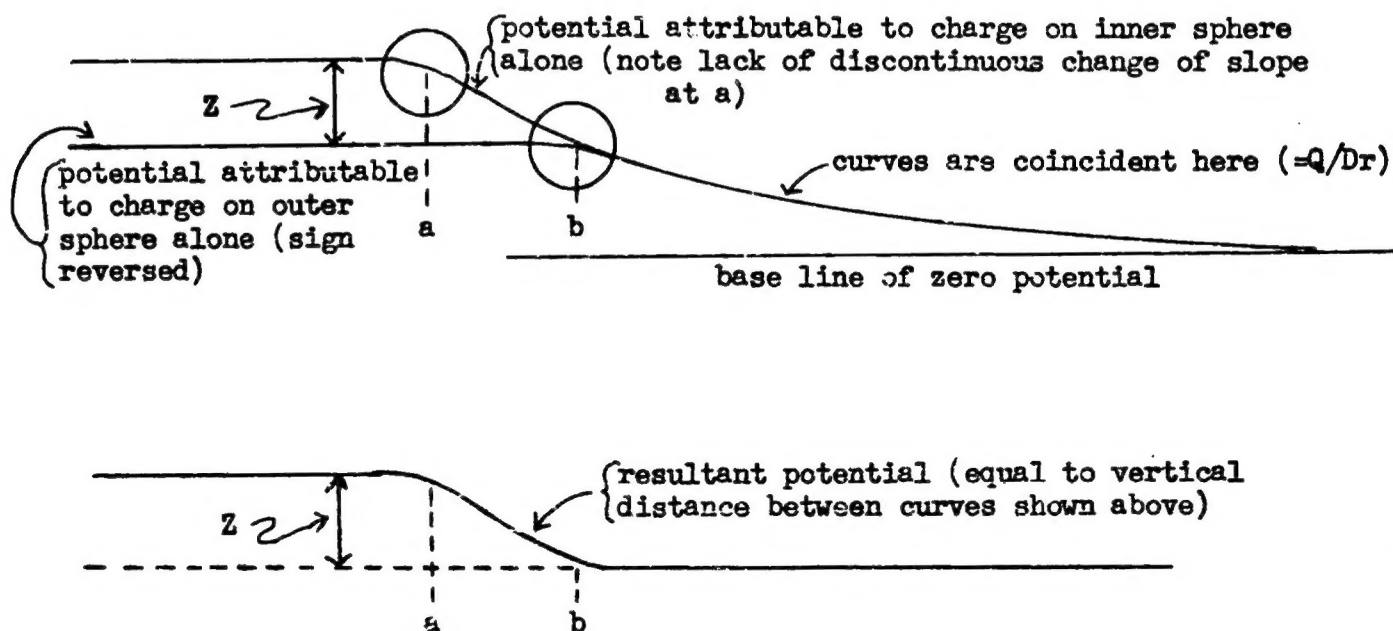


Fig. 5. Schematic representation of potentials attributable to each sphere singly (upper diagram) and the resultant potential (lower diagram) when charges are discrete.

If the distance from b to a is small compared to a , and if the distance between adjacent discrete charges is also small compared to a , then the regions marked by the circles will have nearly identical shapes, becoming identical in the limit as the ratios go to zero. In practice these ratios are both of the order 10^{-7} or less, so that one can assume the curves to be identical in the encircled regions and otherwise identical with Fig. 4. Evidently the potential difference Z is exactly the same as before, namely $QD^{-1}(a^{-1} - b^{-1})$.

These arguments nearly dispose of the contention that the discreteness of charge is responsible for the electrocapillary effects mentioned at the outset of this paper. It is only fair to point out, however, that our arguments have presumed the constancy of the dielectric constant for a region corresponding to all those parts of the electrical double layer lying outside of the metallic phase. This condition is far from being satisfied in reality,

there being three regions of different dielectric constants (presumably) corresponding to the division of the electrical double layer into three regions separated by the inner and outer Helmholtz planes. Some small effects of discreteness of charge can be expected under these circumstances, but it must be admitted that we are far from being able to predict the magnitude of the effects at present. Ershler does divide up the double layer into three regions in the manner we suggest, but his treatment is vitiated, in our opinion, by several circumstances, chief among which is his use of the (somewhat modified) result of Esin and Shikov.²

It will be shown in the following paper that the anomalies which Esin, Shikov, and Ershler are trying to explain are thermodynamically related to another effect which is easily understood without the introduction of discreteness-of-charge effects. The inherent reasonableness of this explanation, coupled with the lack of any real evidence for discreteness effects, compels us to regard as wholly unproved all claims for the detection of such effects in the electrical double layer.

REFERENCES CITED

- (1) O. Esin and V. Shikov, *Zhur. Fiz. Khim.* 17, 236 (1943). Translated by R. Parsons, University College, Dundee.
- (2) B. V. Ershler, *ibid.* 20, 679 (1946). Translated by R. Parsons.
- (3) R. Parsons, Chapter III of "Modern Aspects of Electrochemistry" (Edited by J. O'M. Bockris), Butterworths (1954). In press. Section 4 iii v.

The author is deeply grateful to Dr. R. Parsons for copies of the translations mentioned above and also for an advance copy of Chapter III of the forthcoming book listed as reference 3.

December 31, 1953

² According to Ershler the work ψ_A done against electrical forces for adsorption (of a dipole?) within a dipole layer such as that shown in our Fig. 1 is $0.74 \psi_0 \gamma e / b$ where ψ_0 is the potential difference calculated on the assumption of smeared out charges, γ and e are as defined in the text above, and b is the mean distance between adjacent dipoles. According to this equation ψ_A depends upon γ/b , which is reasonable, but it increases without limit as b goes to zero (γ being constant), which is unreasonable since this is the condition which corresponds to a uniform smeared out charge. It must also be mentioned that ψ_A , as defined above, would not appear to be the quantity of interest for these calculations anyway.

NOTE ADDED JANUARY 5, 1954

It can be shown that even in a system of variable dielectric constant there should be no discreteness-of-charge effect. Perhaps the simplest proof of this statement comes from noting that use of a dielectric constant different from unity is only a device for obviating the necessity of taking into explicit account the orientation of dipoles of the medium. When this orientation of dipoles is expressly considered, the dielectric constant of any medium is unity and therefore constant. So the proof we have presented above applies to all of the many layers of discrete oriented dipoles, including those of the solvent medium itself.

In the particular case of the electrical double layer at a metal-solution interface it is convenient to regard the metal as a medium of infinite dielectric constant and the solution as a medium of dielectric constant unity. Then every charge and every dipole will have its mirror image in the metal, and the system may be replaced by one composed of the double layer and its image, with dielectric constant unity throughout. The actual potential difference between the solution and the metallic surface will then be just half that between two points far removed from the surface and lying on opposite sides of it.

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A numerical calculation based upon equation 1 has been carried out in an effort to verify in a particular case the theorem stated in the main part of this paper. The results are compatible with the theorem, but the convergence of the series was so slow that one could not say with conviction that the theorem had been verified numerically. The work was stopped when it became apparent that the logical foundations of the theorem were so firm that a numerical verification could not add anything to them.

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For additional comments on the Esin-Shikov-Ershler theory, see page 4 of the following paper. It is possible that these authors were thinking, not of the discreteness-of-charge effect which is calculated in the foregoing paper, but of the effect of the crowding of the ions of the adsorption layer by the entrance of further charge. It is true that this is a discreteness-of-charge effect, since it goes to zero when the elementary charge on an ion is supposed indefinitely reduced. In all practical cases, however, it is

already negligible for ionic charges as they actually are.

To show that this is so, consider a sphere of radius r and charge Q to which there is added a unit charge e . The increase in the energy of the system is given by

$$\frac{C}{2}(E_2^2 - E_1^2) = \frac{r}{2} \left[\frac{(Q + e)^2}{r^2} - \frac{Q^2}{r^2} \right] = \frac{eQ}{r} + \frac{e^2}{2r} \quad (4)$$

where C is the capacity of the sphere ($= r$). The first term, eQ/r , is the work needed to move the charge e up to the sphere; hence the second term, $e^2/2r$, is the work needed to "make room for" the entering charge by compressing the charge already present. This term is $e/2Q$ times larger than the first term, so that its neglect produces an error in the calculated work of $1/2n$ where n is the number of unit charges already on the sphere. In any actual experiment, n is at least 10^{10} , so that the error arising from its neglect will be altogether negligible. There is no reason to suppose that the result of this calculation will be significantly altered by taking into account the discrete nature of the charge already on the sphere.

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THE APPARENT ANOMALY IN THE RATE OF CHANGE WITH CONCENTRATION OF THE
POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM

by

David C. Grahame

ABSTRACT

It is known that the rate of change with concentration of the potential of the electrocapillary maximum sometimes exceeds the maximum value considered possible in terms of classical concepts. The supposed anomaly is here reexamined and found to arise from a chemically induced dipole potential which acts between the metallic surface and the inner Helmholtz plane. The thermodynamic significance of the supposed anomaly is investigated and found to correspond to the occurrence of negative values of τ_+ , the transference number of the cation in the double layer. The electrostatic significance of the result is discussed.

EXPOSITION OF THE PROBLEM

It was first pointed out by Esin and Markov (1) that the potential of the electrocapillary maximum (e.c.max.) of mercury varies with the chemical potential of a 1:1 electrolyte with which it is in contact at a rate which sometimes exceeds $1/2F$ where F is Faraday's constant. Explicitly what they pointed out was that the potential of the e.c.max. of mercury in contact with aqueous solutions of potassium iodide varied at a rate somewhat in excess of 59 millivolts per tenfold change of concentration of the electrolyte. The potential of the e.c.maxima in question was always referred to a constant reference electrode, so that liquid junction potentials were involved in the measurements, but these are small enough to be of no consequence in the argument which follows.

In order to understand why a value of $(dE/d\mu)^{e.c.max.}$ greater than $1/2F$ was regarded as anomalous, consider the distribution of a capillary-active anion such as iodide ions between the solution and the inner Helmholtz plane, the plane of the electrical centers of the adsorbed ions. Let w be the work needed to move the ion from the interior of the solution to a place on the surface. Then the charge density of the adsorbed anions, η_-^i , will be proportional to the concentration c_i of anions in the solution and

to a Boltzmann factor $\exp(-w_1/kT)$. Calling the proportionality factor B

$$\eta_-^1 = B c_1 \exp(-w_1/kT). \quad (1)$$

The work w_1 may be represented as the sum of two terms, the first representing the work which must be done against purely electrical forces in the double layer and the second representing the work done by specific forces of attraction, short range in character, and essentially chemical in nature. Thus*

$$w_1 = z_- \epsilon (\psi^1 + \phi_-^1) \quad (2)$$

and

$$\eta_-^1 = B c_1 \exp[-z_- \epsilon (\psi^1 + \phi_-^1)/kT] \quad (3)$$

In these equations z_- is the valence of the anion, including sign, and ϕ_-^1 is the specific adsorption potential of the anion expressed in electrical units. It is a function of the charge on the metallic surface (2). ϵ is the unit of electrical charge.

It will facilitate discussion to write equation 3 in the form

$$c_1 = (\eta_-^1/B) \exp(z_- \epsilon \psi^1/kT) \exp(-\phi_-^1/kT) \quad (4)$$

In the presence of a capillary active anion and at the potential of the e.c.max. ψ^1 is always negative, and becomes more negative as c_1 increases. Thus the exponential containing it increases. It is confirmed by experiment (2), what one would certainly anticipate, that η_-^1 increases with c_1 . The specific adsorption potential is primarily a function of q , the electronic charge density on the metallic surface, which is constant and equal to zero at the potential of the e.c.max., but it is probably also to some very minor extent a function of η_-^1 , which is proportional to the surface coverage. Since the actual fraction of the metallic surface covered by anions is always small at the e.c.max., usually less than ten percent by current estimates, it is unlikely that ϕ_-^1 changes appreciably with changes in c_1 , q being held constant. In so far as ϕ_-^1 changes at all, it is expected to decrease with increasing η_-^1 , and so with c_1 . This means that the exponential $\exp(-\phi_-^1/kT)$ in equation 4 will either remain constant or

*Essentially the same argument up to this point appears in ref. 2, p. 485. It is a restatement of parts of the theory of Stern (3). The sign preceding ϕ_-^1 has been reversed from that appearing in these references in the belief that less confusion will result if ϕ_-^1 is defined in such a manner that it is always positive or zero, never negative. Thus a strong adsorption will always correspond to a large positive value of ϕ_-^1 .
Footnote continued on page 10.

increase slightly with increase in c_1 .

To sum up, all three factors on the right of equation 4 increase (or in the case of the last factor, possibly remain constant) with increase in c_1 . Thus a tenfold increase in c_1 must be divided among the three factors on the right in such a manner that no one factor can increase more than tenfold. In practice η_-^1 increases about twofold, on the average, and $\exp(z_- \epsilon \psi^1/kT)$ will therefore increase by about fivefold, or possibly a little less, depending upon the constancy of $\exp(-\phi_-^1/kT)$. A tenfold increase in $\exp(z_- \epsilon \psi^1/kT)$ corresponds to a 59 millivolt increase in the absolute magnitude of ψ^1 at 25°C for a univalent ion. Thus ψ^1 cannot possibly increase by more than this amount for a tenfold change of c_1 .

It is a consequence of the theory of Stern (3), or of simple electrostatic considerations (4), that when q is zero (i.e. at the potential of the e.c.max.), the potential of the metallic phase ψ^M is the same as that of the innermost layer of charge, the inner Helmholtz plane, ψ^1 . This statement intentionally neglects the potential difference developed by oriented solvent molecules on the grounds that this difference remains essentially constant and does not influence any of the properties with which we are here concerned. Potentials defined in this way have been termed by the author "rational potentials" (2). In any case changes in ψ^M should equal changes in ψ^1 when q is kept equal to zero. It will be shown later that this statement is not really true, but for the moment we are concerned with showing why it was originally expected to be true.

When q is zero the slope of the potential-distance curve is zero by Gauss' law for systems in which the charge density is a function of only one distance variable, x . This is true regardless of the dielectric constant of the medium and regardless of the possible presence of charged layers elsewhere in the system. Thus it seems natural to conclude, as Stern did, that $\psi^M = \psi^1$. It is even more natural to conclude that

$$\Delta \psi^M = \Delta \psi^1 \quad (5)$$

where the Δ refers to change occurring at $q = 0$.

Nevertheless this leads to a contradiction with experiment. We have already seen that a tenfold change in c_1 may cause a change in $\Delta \psi^M$ exceeding 59 millivolts, whereas equation 4 sets an upper limit to $\Delta \psi^1$ of 59 millivolts with the expectation of considerably less because of the expected (and observed) increase in η_-^1 .

PREVIOUS ATTEMPTED EXPLANATIONS

Esin and Shikov (5) have attempted to explain this contradiction by denying the validity of equation 5. With this we are in agreement, thus reversing our earlier expressed opinion (2,4). Esin and Shikov attribute the failure of equation 5 to the discreteness of charge of the adsorbed anions, and make a calculation of the work needed to move a pair of oppositely charged ions into the double layer. Ershler (7) made a more extensive calculation based on a more realistic model of the electrical double layer, but continued to use the basic equation of Esin and Shikov. In both papers it is assumed that the work needed to move a pair of ions into the double layer is reflected in the external potential difference observed at the e.c.max. This concept is superficially reasonable, but on detailed examination appears to us to be without foundation since the thermodynamic process to which the potential corresponds is not the addition of a pair of ions to the double layer.

THERMODYNAMIC CONSIDERATIONS

The argument presented above assumes that liquid junction potentials are not large enough to resolve the contradiction. This assumption can be strengthened by showing that the contradiction exists even in the absence of liquid junctions and their concomitant potentials.

It has been shown in a recent publication (8) that the potential of a polarized electrode E^- varies with the chemical potential of the electrolyte μ according to the equation

$$z_+ v_+ F (\partial E^- / \partial \mu)_q = \tau_+ \quad (6)$$

where τ_+ is the "transference number" of the cation in the electrical double layer, a measure of the fraction of the total charge carried into the double layer by the cations in an infinitesimal change of applied potential E^- . v_+ is the number of cations formed by the dissociation of one molecule of the electrolyte. E^- is the potential measured relative to an electrode reversible to the anion of the electrolyte. As the concentration of the electrolyte changes, so does the concentration of the electrolyte in the reference electrode. Thus liquid junction potentials are absent.

Values of τ_+ are available in several ways. Equation 6 is itself one source. τ_+ is also given by $d\bar{q}_+/dq$ (its defining equation) or by C^+/C , where C is the differential capacity of the double layer and C^+ is the

part of C attributable to cations. Γ_+ is the charge attributable to the excess of cations in the double layer. Values of Γ_+ are given in ref. 2 and 8. Values of C^+ and C are to be found in ref. 8. Curves of Γ_+ vs. E usually show a minimum (2,8) at which potential $d\Gamma_+/dq = 0$ and therefore $\tau_+ = 0$. At potentials more anodic than this, τ_+ is negative, corresponding to the fact that increasing the positive charge on the metal increases the concentration of anions by more than an equivalent amount, the difference being made up by cations moving into the double layer. Thus they flow in a direction contrary to that of the total flow of positive current.

This phenomenon has been discussed several times previously (2, 8, and other references there cited) and arises from the fact that the strength of the chemical bond which holds the anion to the metallic surface increases with increasing positive charge (see Fig. 15 of ref. 2). This fact will be employed in the argument of the next section.

The subscript q in equation 6 denotes the constancy of the surface charge density. At the e.c.max. $q = 0$ and equation 6 becomes

$$(dE^-/d\mu)^{e.c.max.} = \tau_+^{e.c.max.}/F \quad (7)$$

Here we have set $\nu_+z_+ = 1$, corresponding to a 1:1 electrolyte. This will simplify the discussion which follows. There is no difficulty in carrying through the corresponding discussion for other valence types, however, (see footnote 14 in ref. 8).

For electrolytes which exhibit specific adsorption on mercury (which seems to include nearly all salts except fluorides), and in the cases which have so far been studied, Γ_+ reaches a minimum at a potential which is on the anodic side of the potential of the e.c.max. for very dilute solutions, shifting gradually to the other side as the concentration is increased. Thus there is usually, perhaps always, a concentration where $\tau_+ = 0$ at the e.c.max.* This condition is reached, for example, in 0.3 M NaCl (2). This condition furnishes a particularly clear example of the seeming contradiction with which this paper is concerned.

Under the conditions in question $(dE^-/d\mu)^{e.c.max.} = 0$. Thus the overall potential difference from polarized electrode to reference electrode is unchanging with concentration, and since the reference electrode is

* It will be recalled that $\tau_+ = 0$ when Γ_+ reaches a minimum.

reversible to the anion, the polarized electrode must be changing its potential relative to the solution as if it, too, were reversible to the anion. That is to say, ψ^M must be changing by 59 millivolts for every tenfold change in the activity of the anion.* Since η_{-}^i is also increasing with concentration, ψ^i cannot increase by as much as 59 millivolts, hence $\Delta\psi^M \neq \Delta\psi^i$, contradicting equation 5.

The contradiction becomes increasingly great as the concentration of the electrolyte is taken greater, making τ_{+} negative by ever increasing amounts. Then the polarized electrode changes its potential with concentration even faster than does the reference electrode. It behaves, in fact, like an electrode reversible to an anion carrying a charge of $2\tau_{+} - 1$.

It is of particular interest that the contradiction becomes greater as the concentration increases. This is not the behavior expected of a system which is showing a discreteness-of-charge effect. For as the concentration of the electrolyte increases, so does that of the adsorbed ions, and the layer of charge becomes more nearly continuous. It is also significant that at very low concentrations, or at moderate concentrations of less strongly adsorbed anions, $\tau_{+}^{e.c.max.}$ approaches its limiting value $1/2$. Thus under conditions where discreteness-of-charge effects might be expected to be most prominent, they disappear altogether.

PROPOSED EXPLANATION OF THE CONTRADICTION

Although it is true that thermodynamics cannot be adduced in support of an explanation of mechanism, thermodynamics coupled with experimental data may make the facts so clear that the explanation becomes almost self-evident. That appears to us to be the situation here.

The contradiction we are seeking to explain is associated with zero or negative values of $\tau_{+}^{e.c.max.}$. But there is no difficulty in understanding these values of $\tau_{+}^{e.c.max.}$, and one has only to translate this explanation into the language of electrostatics to find the error in the reasoning associated with the electrostatic problem.

This error is as follows: It was assumed that the non-coulombic (chemical) forces acting on the adsorbed anion could not give rise to a displacement of charge above and beyond that taken into account explicitly in

* Strictly speaking one should say that $(d\psi^M/d\log_{10} a)^{e.c.max.} = 0.059$ v.

connection with the electrostatic potential ψ^1 . That this is not so is recognized clearly enough for uncharged molecules (especially for the solvent molecules), but it has been consistently overlooked for charged molecules (ions), probably because it was felt that this effect was implicitly taken care of by the coulombic potential term. This is not so, as is shown most clearly by the contradiction to which it leads and also by a closer scrutiny of the assumption itself. The forces acting on the ion are in part chemical, meaning that a displacement of charge occurs which is not the result of those charges which are taken into account explicitly by double layer theory. While it is true that chemical forces are electrostatic in origin, they are not taken account of fully by the introduction of an adsorption potential ϕ^1 . What is omitted is all consideration of chemically induced dipoles lying between the metallic surface and the inner Helmholtz plane. The displacement of charge mentioned above effectively generates such dipoles which are responsible for a potential difference $\psi^M - \psi^1$ at the e.c.max., and no doubt at other potentials as well. It is interesting to note that the negative end of the dipole is directed towards the metal, as one would expect of a chemical bond in which both of the shared electrons are provided by the anion.

EVALUATION OF ψ^1

There is as yet no straightforward method of evaluating ψ^1 . Until now the difficulty has been compounded by the unresolved contradiction with which this paper is concerned. Now that this contradiction is seemingly resolved, it is possible to proceed on the basis of reasonable conjecture, whereby we may hope to achieve a semi-quantitative understanding of the properties of the electrical double layer, including an evaluation of ψ^1 . Although it is not the purpose of this paper to pursue the intricacies of such an evaluation, we shall outline the procedure which currently appears to us most reasonable.

The differential capacity C^0 of the region between the metallic surface and the outer Helmholtz plane can be found by use of the equation (ref. 2, eq. 53)*

$$C^0 = C^d / (C^d - C) \quad (8)$$

*As mentioned in reference 2, this equation is strictly valid only in the absence of specific adsorption.

where C^d , the differential capacity of the diffuse double layer is given by the equation (ref. 2, eq. 47)

$$C^d = (zeA/kT) \cosh ze\psi^0/2kT. \quad (z:z) \quad (9)$$

Here ψ^0 is the potential relative to the interior of the solution of the outer Helmholtz plane and z is the absolute value of the valence of the ions of an electrolyte of symmetrical valence type. A is a constant defined in reference 2, page 474.*

η^d , the charge in the diffuse double layer, is given by the relation (ref. 2, eq. 43)

$$\eta^d = -2A \sinh ze\psi^0/2kT. \quad (z:z) \quad (10)$$

Elimination of ψ^0 between equations 9 and 10 gives a useful relation which seems not to have been published heretofore, namely

$$C^d = (ze/2kT) \left[(\eta^d)^2 + 4A^2 \right]^{\frac{1}{2}} \quad (z:z) \quad (11)$$

In the absence of specific adsorption, $\eta^d = -q$, which makes it easy to find C^d and hence also C^o for such electrolytes. In the presence of specific adsorption η^d can still be found (2,3), and it will be assumed that C^o still retains its value as a function of η^d as if specific adsorption were absent. More precisely, it can be assumed that the part of the double layer lying between the inner and outer Helmholtz planes has the same differential capacity C^{oi} for a given value of η^d (at the same salt concentration) whether or not anions are present in the inner Helmholtz plane. This assumption appears to be so plausible as to be almost axiomatic. Its usefulness is somewhat diminished by the fact that one never actually knows the magnitude of C^{oi} even in the absence of specific adsorption. One might, however, proceed as follows:

It is known that when $\tau_+ = 0$, $C = C^i$ (ref. 2, p. 468), and the considerations advanced in this paper in no way contradict that assertion. Then if we write rather formally

$$C^o = C^i C^{oi} / (C^i + C^{oi}) \quad (12)$$

(i.e. regarding C^i and C^{oi} as two capacitances in series), it is possible

*A typographical error appeared in the original printing of the definition of A . The correct equation is $A^2 = (DD_0 kT n_{oi} / 2\pi)$.

to find C^{oi} where $\tau_+ = 0$. In using this equation C^o will need to be taken from results obtained with a capillary-inactive electrolyte, say potassium fluoride. The cation should in any case be the same as that for the salt whose anion adsorption is under investigation. Equation 12 is not to be interpreted too literally and probably should not be employed with concentrated solutions of strongly capillary-active electrolytes. It is easy to prove that equation 12 is correct in the complete absence of specific adsorption. Its use can also be justified when specific adsorption is present, provided the latter is small, as when $\tau_+ = 0$.

In particular, it would always be possible to use equation 12 to find C^{oi} at low concentrations. Then if C^{oi} is assumed to be a function of η^d only, as seems probable, and not of salt concentration, good values of C^{oi} can be obtained. This is the preferred method when the data are available. Our final assumption will be that $1/C^{oi}$ is always the same fraction of $1/C^o$ for a given electrolyte. In effect this assumes that $\psi^M - \psi^i$ is always the same fraction of $\psi^M - \psi^o$ when specific adsorption is virtually absent. The reasonableness of this assumption is apparent. This assumption then suffices to permit the calculation of C^{oi} .

The formal definition of C^{oi} is

$$C^{oi} = d\eta^d/d(\psi^i - \psi^o) \quad (13)$$

whence by integration one obtains $\psi^i - \psi^o$ except for a constant of integration. The latter is found by considering that $\psi^i - \psi^o$ is the same fraction of $\psi^M - \psi^o$ as C^{oi} is of C^o at any cathodic potential where specific adsorption of anions is small.

This somewhat lengthy sequence of calculations appears to be feasible and the underlying assumptions appear to be sufficiently plausible to warrant the effort. It is hoped that the results of such calculations can be reported in a future paper.

It is evident that a calculation of ψ^i will permit the calculation of ϕ_-^i through equation 3. It is expected that ϕ_-^i will be a function of q and (slightly) of η_-^i but not of c_1 , the concentration. If these expectations are borne out, the theory may be said to have survived its first experimental test.

SUMMARY

It has been shown that the anomalous variation with concentration of the potential of the e.c.max. is associated with zero or negative values of τ_+ . These in turn are associated with the presence of chemical forces (bonds) acting between the metal and the chemisorbed anions. In terms of electrostatics it is clear that these bonds give rise to dipoles lying between the metallic surface and the inner Helmholtz plane, and that this is the source of the "extra" potential which had heretofore been neglected.

The resolution of this anomaly has made it possible to see more clearly how one might hope to evaluate the potential ψ^i of the inner Helmholtz plane.

REFERENCES CITED

- (1) O. Esin and B. Markov, *Acta Physicochim.* 10, 353 (1939).
- (2) D. C. Grahame, *Chem. Rev.* 41, 441 (1947).
- (3) O. Stern, *Z. Elektrochem.* 30, 508 (1924).
- (4) R. B. Whitney and D. C. Grahame, *J. Chem. Phys.* 9, 827 (1941).
- (5) O. Esin and V. Shikov, *Zhur. Fiz. Khim.* 17, 236 (1943).
- (6) D. C. Grahame, preceding paper.
- (7) B. V. Ershler, *Zhur. Fiz. Khim.* 20, 679 (1946).
- (8) D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.* 22 (1954). In press.

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Continuation of footnote from page 2. The symbol ψ^i denotes the electrical potential of the inner Helmholtz plane, which is the locus of the electrical centers of anions which are specifically adsorbed.